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Nanotechnology: Quantum Dots and Carbon Nanotubes

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EVOLUTION OF NANOTECHNOLOGY

Over the last decade, the electronics industry has witnessed a drastic decrease in the size of circuit component size, fueled by the need for increased complexity and performance. As the size of these components decrease, quantum mechanical effects become increasingly important. A device reaches the quantum size effect when the size of the device is comparable to electron wavelength. In this regime, classical physics fails to describe the phenomena that occur in these devices. Quantum well and quantum cascade lasers are just a few examples of the realization of quantum mechanics. The area of quantum dot physics and devices is relatively new, and has several applications in bio-engineering.

Recent developments in semiconductor quantum-dot (QD) technology nanostructures have opened up new possibilities in the area of nanotechnology. One example is a "Quantum Dot", which has extraordinary electrical, optical, and mechanical properties. Carbon nanotubes are another recent development in nanotechnology. Carbon nanotubes have been the topic of much research, and they hold the potential for many biological and medical applications in the future.

CREATION OF QUANTUM DOTS

There are two basic methods to preparing nanostructures: the bottom-up approach and the top-down approach. The bottom-up approach collects, consolidates, and fashions individual atoms into the desired structure. This can be done by either chemical vapor decomposition or molecular beam epitaxy on a mismatched substrate. To create the quantum dots, a material is layered on a substrate with a mismatching lattice constant. This creates strain between the materials, and quantum dots are formed. This approach has proven to create orderly arrays of self-assembled QDs. The top-down approach, also known as lithography, is just the opposite. Lithography requires starting with a large-scale object and gradually reducing the dimensions to the size specified. The first step involves coating a photon or electron-beam-sensitive resist on a substrate and lithographically exposing it to a beam of electrons. Then, a developer is applied to remove the irradiated portions of the resist, and a layer of either metal or dielectric etch mask is deposited everywhere on the structure. Next, the remaining parts of the resist are lifted off. Lastly, the areas of the quantum dot not covered by the etch mask are chemically etched away (Poole). Using this technique, complex nanostructures such as quantum dot arrays can be created.

Quantum dots form during the epitaxial growth of two semiconductors having two different lattice constants. The most common system consists of InAs dots grown on a GaAs substrate. Here, there is a 7% difference between the lattice constants. A mono atomic layer of InAs is deposited on the GaAs using molecular beam epitaxy or metal organic vapor phase epitaxy (MOVPE). The lattice strain continuously builds up to form three-dimensional growth in the form of islands. It has been experimentally shown that these islands usually form in a pyramidal shape (Jiang 1188). Typically the dimensions approach 100x70 Å, and the packing densities approach about 70 Å. These islands form the Quantum dots, which have high optical quantum efficiency (Chakraborty).

USING QUANTUM DOTS IN BIOLOGICAL ENVIRONMENTS

To functionalize QDs in biological environments, there are two problems that need to be solved: making QDs fluoresce in aqueous environments, and conjugating them to specific bio-molecules. A common solution to the first problem involves coating CdSe QDs with trioctylphophine oxide (TOPO) or mercaptoacetic acid (MAA). TOPO enhances the luminance emission of the QDs, but is only soluble in non polar solvents. MAA, on the other hand, allows dissolution in polar solvents, such as water. Semiconducot QDs are, by nature, inorganic materials not compatible with bio-molecules. However, by exploiting the ability of the surface metal ions to bond strongly with other compounds such as sulfur, QDs can become compatible in organic environments. There are many schemes that address this problem. One common solution for functionalizing QDs is conjugating CdS QDs with peptide sequences. Peptide sequences are strings of amino acids which all contain an NH2 group bound to COOH group by a carbon atom. This carbon atom is bounded to a hydrogen atom and a side-group, which distinguishes one amino acid from the other. A thiol compound, which contains and sulfur soluble compound, forms a shell around the QD so that it may be dispersed in water (Leon, 3186). Another method for conjugating quantum dots with bio-molecules involves the covalent bonding of a carboxyl group in a ligand to a carboxyl group on the bio-molecule. This is useful because the carboxyl group is very common in a wide variety of molecules such as proteins, antibodies, and DNA. One of the most useful QD conjugates is called Streptavidin because it stabilizes the particle and provides a link between the QD and bio-molecules.

The role of peptide selectivity in the binding of QD complexes to cells has been examined by Alexons. Specifically, the α3β1 integrin was examined, which existed in most tumor cells. Also, MDA-MB-435 cells have a high level of the αvβ3 integrin. To verify that the bindings did in fact occur, the MDA-MB-435 cells were exposed to CGGGRGDS and CGGGRVDS functionalized CdS QD complexes. From results indicated in Alexson's paper, it is clear that the CGGGRDGS based QDP complexes bind to the MDA-MB-435 cells while the CGGGRVDS based quantum-dot-peptide (QDP) complexes do not. These findings show the selectivity of peptides to the binding of QDP complexes to MDA-MB-435 cells. Also, it shows that there are unique peptides that link to unique QDP complexes.

Multicolor fluorescence using Quantum Dots: Realization and Application

Bio-imaging is one of the most notable applications of this nanotechnology. This technology offers many advantages over fluorescence microscopy, which is a well established method for high-resolution biological imaging. Some of the drawbacks to fluorescence microscopy include sensitivity to environmental changes, such as pH, photo bleaching, Stokes shifts, and fixed emission spectra (Alexson R637). Quantum dots, on the other hand, are more robust and have the capability of inducing multicolor fluorescence with a single wavelength excitation source (Leon 3186). This is possible because there is energy loss due to lattice vibrations and transitions between the excited states and the ground state. Therefore, the wavelength of the re-emitted light may be longer than the wavelength of the light source. The specific wavelength that the QD emits is dependent on the energy gap of the semiconductor and the physical size of the QD. The following table shows some common nanocrystals and the relationship between diameter and the emission peak wavelength (Leon 3186).

Nanocrystal	Size (diameter nm)	Emission peak (nm)
Bare CdSe	3.9 +/- 0.4	575 (green)
Bare CdSe	4.6 +/- 0.4	587 (yellow)
Bare CdSe	5.4 +/- 0.4	615 (red)
Core shell CdSe/ZnS	3.6 +/- 0.3	565 (green)
Core shell CdSe/ZnS	6.5 +/- 0.5	620 (red)

Also, one should note that the sizes of these nanocrystals can be continuously and precisely tuned to obtain the desired wavelength. Figure 1 is an example of quantum luminescent dots.

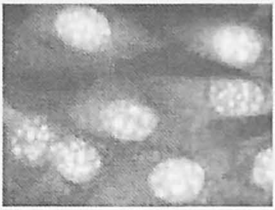

Figure 1: Quantum luminescent dots (Evidenttech)

The applications of QDs in bio-photonics are not limited to bio-imaging. These nanostructures can also be used in bio-sensors, which fluoresce only in the presence of living organisms. These kinds of sensors are useful for "life detection" experiments on earth, or even other planets. Traditionally, fluorescent dyes are introduced into a soil, or other substance, and then excited with a light source. However, there are a few obstacles when using these dyes. Most dyes are organic and are sensitive to sterilization procedures as well as radiation bombardment and freeze-thaw. These sensitivities become of particular interest when dealing with non stable environments, such as space-flight. Biologically compatible QDs, however, look promising as a viable alternative to these dyes. In addition, space-flight often requires minimal space, mass, and energy considerations. Miniature lasers can be used as an excitation source for semiconductor nanocrystals and, as a result, are ideal for space applications (Leon 3186).

FUTURE APPLICATIONS OF QUANTUM DOTS

Quantum dots can be used in many different areas, including liquids, fabrics, and polymers. Today, special dyes are often used as an anti-counterfeiting measure. These dyes may soon be replaced by quantum dot technology because of their superior versatility and tunability features. LED's are another technology that may soon be replaced by quantum dot LED's. The company Evident Tech is developing QLED™, an LED that will be tunable to any visible or infrared wavelength and can be fabricated into many different materials (Evidenttech). The same company is also working on a product called Evidust. Quantum dots can be made to look like ordinary dust and have the ability adhere to a person. However, unlike ordinary dust, QDs can be specified to emit infrared radiation at a desired wavelength. Therefore, they would act as good tracking devices or even as an anti-trespass device. One last application of QDs involves doping glasses and polymers with Quantum dots to change their optical qualities. Because QDs are semiconductors, they have the ability to change their electron population when exposed to a stimulus. This allows for the ability to change the absorption coefficient and refractive index by altering the power input to the QDs (Evidenttech).

CARBON NANOSTRUCTURES

Carbon nanostructures are an important field of study because the carbon atom and the carbon bond are essential to the molecules of life. The carbon nanotube (CN) is certainly the biggest recent discovery in this field. A carbon nanotube is a concentric tube consisting of carbon-atom hexagons that are arranged in a helical fashion (Chakraborty). The diameter of CN's is usually between 20 and 300 Å and the length can exceed 1 μm. Figure 2 is a computer generated image of a carbon nanotube.

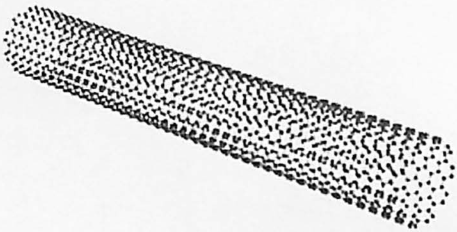

Figure 2: Carbon Nanotube (Royal Society)

The synthesis of CN's usually results in both metallic and semiconducting tubes, depending on the arrangement of the atoms. To describe the chirality of the tube, a chiral vector is often used. This vector consists of two integer values, n and m, which describe how the graphene sheet is wrapped along the T axis. These integers denote the number of unit vectors along two directions in the crystal lattice of the graphene. Two common nanotubes are "zigzag" with m = 0 and "armchair" with a chiral vector of n = m. Suppose a nanotube is described by the ratio:

$$\frac{n-m}{3}$$

where n and m are integer values.

If this ratio is an integer value, then the single walled carbon nanotube (SWNT), will be metallic. Otherwise, it will be a semiconductor. For example, nanotubes (5,0), (6,4), and (9,1) are all semiconductors. From this relationship, it is clear that the chirality is the key factor in determining the properties of carbon nanotubes.

Figure 3 is a representation of the graphic plane. In this figure, T represents the tube axis, and a1 and a2 are the unit vectors of the graphene.

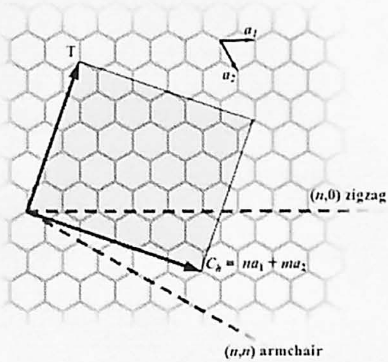

Figure 3: Graphic Plane (Wikipedia)

Mechanical and Thermal properties of Carbon Nanotubes

Carbon nanotubes have a variety of properties that make them unique. One interesting property is that they exhibit very good thermal conduction along the direction of the tube, but act as an insulator laterally to the tube axis. Also, like any other material, nanotubes are weakened by defects in the material. A given defect can reduce the strength of the tube by as much as 85% (Wikipedia). However, carbon nanotubes can be created so that they have barely any defects. Therefore, they are relatively strong and durable. To characterize the flexibility of this material, we can define the stress, S, applied to the tube as:

$$S = Ee$$

where E is Young's modulus and e is the strain defined by:

$$e = \frac{\Delta L}{L}$$

where L is the length of the "wire" before it is stretched.

From these equations, the Young's modulus (E) that characterizes the flexibility of the material can be resolved. Carbon nanotubes have been found to have a Young's modulus ranging from 1.28 to 1.8 TPa—this is about 10 times the Young's modulus of steel. It would appear, then, that CNs would be very stiff (Poole). This is not true, however, because it does not take into account the thickness of tube. Because the tubes are so thin (about .34nm wall thickness), nanotubes are actually very flexible. They can be bent in half and will return to their original shape without any distortion. This is due to the rehybridizing nature of the carbon-carbon sp^2 bonds. In addition, carbon nanotubes are extremely strong. Their tensile strength is about 45 billion pascals compared to the 2 billion pascals of a strong steel-alloy material.

ELECTRICAL PROPERTIES OF CARBON NANOTUBES

The electrical properties of semiconductor nanotubes have been studied and show the following results: As the diameter of the tube increases, the bandgap between the valence and conduction band decreases (Poole). This was shown to be a linear dependence relationship. In addition, the electronic structure of nanotubes has been investigated. If one plots the differential conductance (G = I/V) of the tube versus the applied voltage, it is easy to see how close the electron energy levels are to each other. In other words, it is a measurement of the density of states of the electrons.

From these plots, the energy gap can be derived. Looking at the 2nd plot, there is very little current flow for voltages ranging 0 – 7 volts. The bandgap energy of CN is .7eV.

Another interesting characteristic is that these tubes can also be treated as wires in the right scenario. Because of their scale, quantum mechanical effects must be used to describe the electrons. In the quantum mechanical world, particles are treated as both particles and waves. This concept developed because of the discovery of de Broglie's wavelength. This says that:

$$p = \frac{hv}{c} = \frac{h}{\lambda}$$

where p is the momentum of the particle,
h is Planck's constant
c is the speed of light
v is the frequency
and λ is the wavelength.

This equation relates the momentum of a particle with a wavelength, which is associated with a wave. In carbon nanotubes, the only electrons that may pass through must have a de Broglie wavelength that is a multiple of the circumference of the tube. This causes the tube to act like a one-dimensional quantum wire that can be modeled by a potential well having energy of the length of the nanotube (Poole).

APPLICATIONS OF CARBON NANOTUBES

Carbon nanotubes display field emission. In other words, when an electric field is applied along the axis of the nanotubes, electrons are emitted from the ends of the tube. There are several ways that this can be used. One application currently being developed is using these nanotubes to create flat panel displays. Instead of using an electron gun to excite the phosphors on the TV screen, electron emission from the nanotubes can be used to create the image. Another good property of carbon nanotubes is that they are poor transmitters of electromagnetic energy. This is especially important in military applications where there are concerns about electromagnetic pulses damaging equipment.

Field-effect transistors (FET) are yet another possible future application for carbon nanotubes. Experimental carbon nanotube FETs have been shown to exhibit similar conductive properties to silicon FETs. However, nanotubes have the advantage of having a much faster switching rate than silicon counterparts. If these FET's were to be implemented in a computer, it could theoretically have a clock speed of about 10^4 times the speed of current microprocessors. In addition, the use of nanotubes would shrink the size of processors significantly.

Using carbon fiber for reinforcement of materials is fairly common today. This same concept can be applied to carbon nanotubes. For example, research at General Motors has shown that adding nested carbon nanotubes to polypropylene doubles its tensile strength. Also, a study at the University of Tokyo has shown that incorporating 5% carbon nanotubes by volume increases the tensile strength of aluminum by a factor of 2 (Poole).

Lastly, carbon nanotubes have been proposed as components for DNA and protein biosensors, ion channel blockers, and bioseparators and catalysts. Carbon nanotubes are also becoming relevant in neuroscience research and tissue engineering (Bianco 571).

FUTURE OF NANOTECHNOLOGY

As we move into the future, nanotechnology is becoming increasingly important not only in engineering, but in biology and chemistry as well. Advances in the field of semiconductor nanotechnology have and will continue to have a tremendous impact on electronic and optic-electronic devices. Traditional devices have been improved in terms of speed, size, as well as cost. Emerging technologies such as quantum dots and carbon nanotubes hold the potential to revolutionize several areas in optics, electronics, imaging, security, and materials.

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